REACTION OF SPODUMENE WITH ALKALI SULFATES
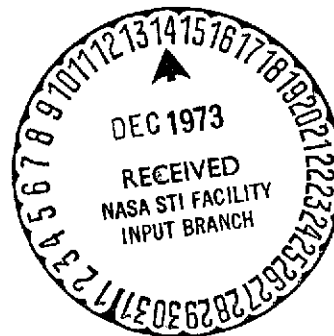
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16. Abstract   If calcined β spodumene is sintered with K_2SO_4, Rb_2SO_4 or Cs_2SO_4, up to 1500°, Li_2SO_4 is formed by ion exchange and is easily leached from the sinter cake. The reaction is incomplete and yield is low with Na_2SO_4. Residual products are leucite, Rb leucite and pollucite. Conversion with K_2SO_4 starts at 700° in the solid phase, and a melt phase forms above 1100°, reducing the amt of Li in the solub.phase. Residual products were identified by X-ray diffraction, optical and differential-thermal methods, the latter indicating enantiotropic inversion effects in leucite and Rb leucite, but no polymorphism in pollucite. Reaction of a 1:1 mix of spodumene and K_2SO_4 starts at 900-950°, but the yield is higher at higher temps. With Na_2SO_4, a viscous glass soon forms, which inhibits and then stops the reaction. For this reason, the use of mixes of both sulfates or of waste salts is unsuitable. Instead of β spodumene concentrate, mine lumps or flotation concentrates can be used. Rapid conversion of the natural α into the high-temp.β modification takes place in the sintering process itself.

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REACTION OF SPODUMENE WITH ALKALI SULFATES

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The possibility of decomposition of lithium minerals
with alkali metal salts had already been established, as a
result of mineralogical research, in the 80s of the last century.
However, the importance of this research for technological
purposes was not recognized at the time. Sintering of lithium
minerals with alkali metal salts, for the purpose of converting
lithium into soluble form, with subsequent production of one
or another of its compounds, was proposed only more than 20
years later. In this case, it developed that better results
are achieved by use of alkali metal sulfates.

Sintering of lithium minerals with K_2SO_4 acquired special
importance, since it had been determined that all lithium
minerals react with K_2SO_4 at temperatures of up to 1500°
(depending on the nature of the mineral), in which Li_2SO_4,
which is easily removed from the sinter cake   with water,
is formed.

A tremendous number of works and patents were devoted to
processing of lithium minerals by sintering with K_2SO_4; however,
particularly much research was carried out on lepidolite and
the major lithium mineral, spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ or
$LiAl[Si_2O_6]$.

The reaction between spodumene and K_2SO_4 proceeds almost
quantitatively, and many investigators have expressed the
opinion that it is a volumetric decomposition, as the result
of which leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ or $KAl[Si_2O_6]$, is formed.
However, this opinion was not supported by any research or
proof, and it was assumed as extremely expedient, the more so

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*Numbers in the margin indicate pagination in the foreign text.

because there is an external mineralogical similarity in the formulas of spodumene and leucite. Moreover, judging by the data in the literature [1-7], the spodumene-K_2SO_4 sintering reaction proceeded completely satisfactorily, and there was no urgent necessity for precisely defining the reaction mechanism.

Meanwhile, it is clear that one assumption of leucite formation from spodumene contradicts old conceptions of ion exchange in the process of the reaction of spodumene with K_2SO_4, similar to that which takes place in the permutite method of water purification. It is completely obvious that, by virtue of the sharp difference in size of the ion radii of lithium (0.78 A) and potassium (1.33 A) and the necessity for carrying out the process at high temperatures, such analogies cannot be recognized as fortunate.

The reaction between spodumene and Na_2SO_4 also has been studied for purely technological purposes, in an effort to replace K_2SO_4 (completely or partially) with Na_2SO_4, which could reduce the cost of the process. However, despite the fact that there are indications [8] of the possibility in principle of replacing K_2SO_4 with Na_2SO_4, even partial replacement of one reagent by the other was completely unjustified in practice at various plants.

The work of Ye.S. Burkser and A.P. Rutman [6] sheds a little light on the reason for failure in replacement of K_2SO_4 by Na_2SO_4. In it, the authors made an effort to study the process of sintering of spodumene with alkali metal sulfates. The sintering was carried out at temperatures a little lower /643 than the melting temperature of the corresponding sulfates, and the amount of the latter in the reaction with spodumene corresponded to a 10% excess over the amount necessary according to the reaction:

It was determined that the action of the sulfates on spodumene increases with increase in atomic weight of the sulfate cation and its ionic radius; in this manner, Na_2SO_4 proves to be the least effective reagent.

The authors of the research were inclined to consider the reaction between spodumene and the sulfates, considering only the pattern of the reacting masses, and they did not study the nature of the solid phase, of the products of this reaction.

Considering that the method for producing lithium compounds, based on sintering spodumene with K_2SO_4, is the one mastered best technologically, it retains its importance up to the present time [9], and it has a number of advantages over other methods and potential possibilities for further improvement, and we undertook initially an investigation of the reaction of spodumene with just K_2SO_4 at high temperatures.

Preliminary study of the reaction between β-spodumene and K_2SO_4, in the 700-1100° range, with various ratios of the components, showed that formation of Li_2SO_4 begins at 700° and proceeds in the solid phase; only above 1100° does the phenomenon of sintering of the particles of the charge yield to the process of melting, which is capable of leading to a decrease in the conversion of lithium to the soluble phase. Sodium (in the form of Na_2SO_4) changes to the soluble form, together with lithium, in sintering β-spodumene with K_2SO_4.

We determined in this case that the clearly expressed ability of β-spodumene to react with various salts at high temperatures is not accompanied by a tendency towards decomposition

of the mineral into a series of phases, with production of soluble aluminates and silicates. Thus, β-spodumene proves to be a convenient initial material for a number of high-temperature syntheses.

Therefore, subsequently, the reaction of spodumene with other alkali metal sulfates was studied by the general method.

The main part of the work was carried out with thermally enriched spodumene (β-spodumene) of the composition: Li_2O 5.44, Na_2O 3.20, Al_2O_3 28.33, SiO_2 62.60 and CaO 0.11 wt-%; K_2O is absent; loss upon roasting 0.2 (Σ = 99.86). The extent of pulverization was such that 90% of the particles of the mineral passed through a 150 mesh sieve.[1]

Investigations of the reactions between β-spodumene and alkali metal sulfates was carried out with various ratios of the components, variable duration of sintering and over a wide range of temperatures.

In all tests, the spodumene was thoroughly mixed with calculated quantities of a pure sulfate (Me_2SO_4), and the prepared mixture was then transferred to corundum-coated crucibles, in which they were placed in a muffle furnace, heated to the prescribed temperature. Upon completion of the test, the contents of the crucibles were repeatedly treated with water under a rabble, for removal of all soluble salts (the control was by the SO_4^{2-} ion). The solutions from water treatment of the sintered masses contained lithium and sodium (from the spodumene) in all cases, as well as that element, the sulfate of which was in excess to the reaction:

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[1][Translator's note: hundreds digit not clear in text furnished.]

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$$2Li\,[AlSi_2O_6] + Me_2SO_4 + Q_{cal} = 2Me\,[AlSi_2O_6] + Li_2SO_4.$$
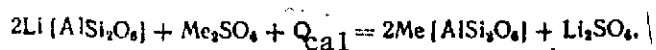
where Me = Na, K, Rb or Cs.

Analysis for the presence of alumina and soluble SiO_2 in the solutions gave a negative result, in the cases of sintering spodumene with K_2SO_4, Rb_2SO_4 and Cs_2SO_4, but not with Na_2SO_4.

The insoluble residues remaining after water treatment of /644 the sinter cake were dried, roasted and subjected to silicate analysis, as well as thermal, optical and x-ray phase examination. As a result of this investigation, it was determined that reaction (2) is of a general nature for the reaction of β-spodumene with alkali metal sulfates having melting temperatures over 1000°: K_2SO_4 (1069°), Rb_2SO_4 (1074°) and Cs_2SO_4 (1019°). In this case, in the absence of melting, the reaction forms Li_2SO_4,(with admixture of other sulfates),and the only insoluble phase is the aluminosilicate of one alkali metal or the other. The aluminosilicates which we synthesized by reaction (2) were identified as leucite, rubidium aluminosilicate (not found as the rubidium analog of leucite) and pollucite (see Table 1).

The formation of new aluminosilicates in the insoluble residues is found by x-ray phase analysis in tests carried out at 900-950°; however, for completion of the reaction (to obtain completely single-phase residues), it is better to carry out the reaction at a higher temperature and with use of excess alkali metal sulfates.

The aluminosilicates, some characteristics of which were given in Table 1, were produced especially under those conditions, in which complete conversion of β-spodumene into other

TABLE 1. DATA ON IDENTIFICATION OF POTASSIUM, RUBIDIUM AND CESIUM
ALUMINOSILICATES PRODUCED BY SYNTHESIS
BASED ON β-SPODUMENE.

Simplest Aluminosilicate Formula	Calculated for the $Me[AlSi_2O_6]$, %	Found for $Me[AlSi_2O_6]$, %	Average Index of Refraction n'	Region and Nature of Thermal Effect on Heating Curve
$K[AlSi_2O_6]$ (leucite)	K_2O 21.59 Al_2O_3 23.36 SiO_2 55.05	K_2O 21,40 Al_2O_3 23,51 SiO_2 55,17	$1,508\pm0,003$	$619 - 640°$ Endothermic, reversible
$Rb[AlSi_2O_6]$ (Rubidium aluminosilicate)	Rb_2O 35.33 Al_2O_3 19.27 SiO_2 45.40	Rb_2O 35,18 Al_2O_3 19,39 SiO_2 45,49	$1,526\pm0,003$	$1055 - 1068°$ Exothermic, irreversible
$Cs[AlSi_2O_6]$ (Pollucite)	Cs_2O 43.72 Al_2O_3 16.77 SiO_2 39,51	Cs_2O 43,60 Al_2O_3 16,90 SiO_2 39,63	$1,514\pm0,003$	Polymorphism absent

aluminosilicates was ensured (temperature 1000°, ratio between β-spodumene and Me_2SO_4 equals 1:1 by weight, which considerably exceeds the amount of Me_2SO_4 theoretically necessary in reaction (2)).

The reaction between β-spodumene and Na_2SO_4 proceeds differently. The initially negligible replacement of lithium in spodumene by sodium increases appreciably, beginning at 900°, owing to the appearance of a melt (Na_2SO_4 melts at 884°). However, the liquation of melted Na_2SO_4 which then sets in, the caking of mineral particles into a rock-like mass and the dissolving of spodumene as such in the Na_2SO_4 melt, with forma-tion of spodumene glass, all lead to retardation of the rate and, finally, to cessation of the reaction. This predetermines the unsuitability of Na_2SO_4 for separate use in production of Li_2SO_4 from spodumene.

We note that the use of mixtures of K_2SO_4 and Na_2SO_4, as well as of waste salts, forming during the lithium compound

production processes and which are low-melting mixtures, can be achieved on a very limited scale. However, of course, it cannot /645 either improve the conditions for stripping spodumene or increase the conversion of lithium to soluble form. The stripping of spodumene by K_2SO_4 always is more effective than stripping with any mixtures, containing a component with an appreciably lower melting temperature than K_2SO_4.

It should be pointed out in conclusion that formation of Li_2SO_4 and insoluble aluminosilicates also proceeds by reaction with alkali metal sulfates of natural spodumene (the α-modification), which was established by special tests. However, the mechanism of the process in this case is such that the reaction of α-spodumene with Me_2SO_4 proceeds through an intermediate stage of conversion of the α- to the β-modification studied previously [10].

The possibility of producing lithium compounds from spodumene in the process of sintering its natural α-modification with K_2SO_4, as is well-known, was used successfully in industry. This possibility is extremely significant for the technology of lithium compounds, since it gives the sulfate process a universal nature, inasmuch as the β-modification is formed in the process itself of sintering α-spodumene with K_2SO_4. In this manner, the sintering of lump spodumene or the flotation concentrate with K_2SO_4 can be accomplished, without resorting to special production of β-spodumene concentrate. This circumstance distinguishes the sulfate method very favorably, for example, from the sulfuric acid method [11], in which only the β-modification of spodumene can be used.

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